

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
28 June 2001 (28.06.2001)

PCT

(10) International Publication Number  
**WO 01/46342 A1**

(51) International Patent Classification<sup>7</sup>: C10G 29/02,  
29/04, 11/02

(US). ROBERIE, Terry, G.; 2613 Liter Drive, Ellicott  
City, MD 21042 (US). ZIEBARTH, Michael, S.; 12071  
Little Patuxent Parkway, Columbia, MD 21044 (US).

(21) International Application Number: PCT/US00/33999

(74) Agents: KEEN, Malcolm, D. et al.; ExxonMobil Research  
and Engineering Company, P.O. Box 390, Florham Park,  
NJ 07932 (US).

(22) International Filing Date:  
15 December 2000 (15.12.2000)

(25) Filing Language: English

(81) Designated States (*national*): AE, AL, AM, AT, AU, AZ,  
BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE,  
ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP,  
KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD,  
MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD,  
SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN,  
YU, ZA, ZW.

(26) Publication Language: English

(30) Priority Data:  
09/468,450 21 December 1999 (21.12.1999) US

(71) Applicant: MOBIL OIL CORPORATION [US/US];  
3225 Gallows Road, Fairfax, VA 22037 (US).

(84) Designated States (*regional*): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian  
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European  
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,  
IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF,  
CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors: CHESTER, Arthur, W.; 517 Country Club  
Drive, Cherry Hill, NJ 08003-3009 (US). DAUGH-  
ERTY, Frederick, E.; 28 Adalisa Avenue, Gibbstown,  
NJ 08027-1302 (US). FUNG, Anthony, S.; 3 Crenshaw  
Drive, Wilmington, DE 19810-3620 (US). KRESGE,  
Charles, T.; 3212 Carriage Court, Midland, MI 48642  
(US). TIMKEN, Hye, Kyung, Cho; 565 Bellvue Avenue  
#23004, Oakland, CA 94608 (US). VARTULI, James,  
C.; 89 Bartlett Drive, Schwenksville, PA 19473 (US).  
KUMAR, Ranjit; 3225 Gallows Road, Fairfax, VA 22037

**Published:**

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.



WO 01/46342 A1

(54) Title: A CATALYTIC CRACKING PROCESS USING A MODIFIED MESOPOROUS ALUMINOPHOSPHATE MATERIAL

(57) Abstract: A process for catalytic cracking of a hydrocarbon feedstock comprises contacting the feedstock with a catalyst composition comprising a primary cracking component, such as zeolite Y, and a mesoporous aluminophosphate material which includes a solid aluminophosphate composition modified with at least one element selected from zirconium, cerium, lanthanum, manganese, cobalt, zinc, and vanadium. The mesoporous aluminophosphate material has a specific surface area of at least 100 m<sup>2</sup>/g, an average pore size less than or equal to 100 Å, and a pore size distribution such that at least 50 % of the pores have a pore diameter less than 100 Å.

BEST AVAILABLE COPY

## A CATALYTIC CRACKING PROCESS USING A MODIFIED MESOPOROUS ALUMINOPHOSPHATE MATERIAL

### BACKGROUND OF THE INVENTION

#### A. Field of the Invention

This invention relates to a catalytic cracking process using a mesoporous aluminophosphate material modified with at least one element selected from zirconium, cerium, lanthanum, manganese, cobalt, zinc, and vanadium. Such materials have high surface area and excellent thermal and hydrothermal stability, with a relatively narrow pore size distribution in the mesoporous range.

#### B. Description of the Prior Art

Amorphous metallophosphates are known and have been prepared by various techniques. One such material is described in U.S. Patent No. 4,767,733. This patent describes rare earth aluminum phosphate materials, which, after calcination, have a relatively broad pore size distribution with a large percentage of pores greater than 150 Å. The typical pore size distribution is as follows:

<u>Pore Size</u>	<u>Volume Percent</u>
50 to 100 Å	5 to 20 %
100 to 150 Å	10 to 35 %
150 to 200 Å	15 to 50 %
200 to 400 Å	10 to 50 %

U.S. Patent Nos. 4,743,572 and 4,834,869 describe magnesia-alumina-aluminum phosphate support materials prepared using organic cations (e.g., tertiary or tetraalkylammonium or phosphonium cations) to control the pore size distribution. When organic cations are used in the synthesis, the resulting materials have a narrow pore size distribution in the range from 30 to 100 Å. When they are not used, the pore size is predominantly greater than 200 Å. U.S. Patent No. 4,179,358 also describes magnesium-alumina-aluminum phosphate materials, materials described as having excellent thermal stability.

The use of aluminophosphates in cracking catalysts is known. For example, U.S. Patent No. 4,919,787 describes the use of porous, rare earth oxide, alumina, and aluminum phosphate precipitates for catalytic cracking. This material was used as part of a cracking catalyst, where it acted as a metal passivating agent. The use of a magnesia-alumina-aluminum phosphate supported catalyst for cracking gasoline feedstock is described in U.S. Patent No. 4,179,358. Additionally, a process for catalytic cracking high-metals-content-charge stocks using an alumina-aluminum phosphate-silica-zeolite catalyst is described in U.S. Patent No. 4,158,621.

There remains a need in the art for highly stable aluminophosphate materials for use in catalytic cracking processes, as well as for simple, safe processes for producing these materials. The aluminophosphate materials preferably possess excellent hydrothermal and acid stability with uniform pore sizes in the mesoporous range, and provide increased gasoline yields with increased butylene selectivity in  $C_4$  gas.

### SUMMARY OF THE INVENTION

This invention resides in a process for catalytic cracking of a hydrocarbon feedstock comprising contacting the feedstock with a catalyst composition comprising a mesoporous aluminophosphate material which comprises a solid aluminophosphate composition modified with at least one element selected from zirconium, cerium, lanthanum, manganese, cobalt, zinc, and vanadium, wherein the mesoporous aluminophosphate material has a specific surface of at least  $100 \text{ m}^2/\text{g}$ , an average pore diameter less than or equal to  $100 \text{ \AA}$ , and a pore size distribution such that at least 50% of the pores have a pore diameter less than  $100 \text{ \AA}$ .

Preferably, the mesoporous aluminophosphate material has an average pore diameter of 30 to  $100 \text{ \AA}$ .

Preferably, the catalyst composition also comprises a primary catalytically active cracking component.

Preferably, the primary catalytically active cracking component comprises a large pore molecular sieve having a pore size greater than about 7 Angstrom.

### DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a process for converting feedstock hydrocarbon compounds to product hydrocarbon compounds of lower molecular weight than the feedstock hydrocarbon compounds. In particular, the present invention provides a process for catalytically cracking a hydrocarbon feed to a mixture of products comprising gasoline and distillate, in which the gasoline yield is increased and the sulfur content of the gasoline and distillate is reduced. Catalytic cracking units which are amenable to the process of the invention operate at temperatures from about 200°C to about 870°C and under reduced, atmospheric or superatmospheric pressure. The catalytic process can be either fixed bed, moving bed or fluidized bed and the hydrocarbon flow may be either concurrent or countercurrent to the catalyst flow. The process of the invention is particularly applicable to the Fluid Catalytic Cracking (FCC) or Thermoform Catalytic Cracking (TCC) processes.

The TCC process is a moving bed process and uses a catalyst in the shape of pellets or beads having an average particle size of about one-sixty-fourth to one-fourth inch. Active, hot catalyst beads progress downwardly cocurrent with a hydrocarbon charge stock through a cracking reaction zone. The hydrocarbon products are separated from the coked catalyst and recovered, and the catalyst is recovered at the lower end of the zone and regenerated. Typically TCC conversion conditions include an average reactor temperature of about 450°C to about 510°C; catalyst/oil volume ratio of about 2 to about 7; reactor space velocity of about 1 to about 2.5 vol./hr./vol.; and recycle to fresh feed ratio of 0 to about 0.5 (volume).

The process of the invention is particularly applicable to fluid catalytic cracking (FCC), which uses a cracking catalyst which is typically a fine powder with a particle size of about 10 to 200 microns. This powder is generally suspended in the feed and propelled upward in a reaction zone. A relatively heavy hydrocarbon feedstock, e.g., a gas oil, is admixed with the cracking catalyst to provide a fluidized suspension and cracked in an elongated reactor, or riser, at elevated temperatures to provide a mixture of lighter hydrocarbon products. The gaseous reaction products and spent catalyst are discharged from the riser into a separator, e.g., a cyclone unit, located within the upper section of an enclosed stripping vessel, or stripper, with the reaction products being conveyed to a

product recovery zone and the spent catalyst entering a dense catalyst bed within the lower section of the stripper. In order to remove entrained hydrocarbons from the spent catalyst prior to conveying the latter to a catalyst regenerator unit, an inert stripping gas, e.g., steam, is passed through the catalyst bed where it desorbs such hydrocarbons conveying them to the product recovery zone. The fluidizable catalyst is continuously circulated between the riser and the regenerator and serves to transfer heat from the latter to the former thereby supplying the thermal needs of the cracking reaction which is endothermic.

Typically, FCC conversion conditions include a riser top temperature of about 500°C to about 595°C, preferably from about 520°C to about 565°C, and most preferably from about 530°C to about 550°C; catalyst/oil weight ratio of about 3 to about 12, preferably about 4 to about 11, and most preferably about 5 to about 10; and catalyst residence time of about 0.5 to about 15 seconds, preferably about 1 to about 10 seconds.

The hydrocarbon feedstock to be cracked may include, in whole or in part, a gas oil (e.g., light, medium, or heavy gas oil) having an initial boiling point above 204°C, a 50 % point of at least 260°C and an end point of at least 315°C. The feedstock may also include vacuum gas oils, thermal oils, residual oils, cycle stocks, whole top crudes, tar sand oils, shale oils, synthetic fuels, heavy hydrocarbon fractions derived from the destructive hydrogenation of coal, tar, pitches, asphalts, hydrotreated feedstocks derived from any of the foregoing, and the like. As will be recognized, the distillation of higher boiling petroleum fractions above about 400°C must be carried out under vacuum in order to avoid thermal cracking. The boiling temperatures utilized herein are expressed for convenience in terms of the boiling point corrected to atmospheric pressure. Resids or deeper cut gas oils with high metals contents can also be cracked using the process of the invention.

The process of the invention uses a catalyst composition comprising a mesoporous aluminophosphate material modified with at least one element selected from zirconium, cerium, lanthanum, manganese, cobalt, zinc, and vanadium. "Mesoporous," as used in this patent application, means a material having pores with diameters in the approximate range 30-100 Å.

Various important properties of the aluminophosphate materials used in the process of the invention have been identified. In particular, the materials should have a specific surface area of at least  $100 \text{ m}^2/\text{g}$ , preferably at least  $125 \text{ m}^2/\text{g}$ , and most advantageously at least  $175 \text{ m}^2/\text{g}$ . Additionally, the materials should have an average pore diameter less than or equal to  $100 \text{ \AA}$ , preferably less than  $80 \text{ \AA}$ , and most advantageously less than  $60 \text{ \AA}$ .

Pore size distribution and pore volume provide other measures of the porosity of a material. In the modified aluminophosphate materials used in this invention, 50% or more of the pores have a diameter less than  $100 \text{ \AA}$ , more preferably 60% or more of the pores have a diameter less than  $100 \text{ \AA}$ , and most preferably, 80% or more of the pores have a diameter less than  $100 \text{ \AA}$ . With respect to the pore volume, the aluminophosphate materials used in the process of the invention preferably have a pore volume in the range from  $0.10 \text{ cc/g}$  to  $0.75 \text{ cc/g}$ , and more preferably within the range of  $0.20$  to  $0.60 \text{ cc/g}$ .

The mesoporous aluminophosphate materials used in the process of the invention are synthesized using inorganic reactants, water and aqueous solutions and in the absence of organic reagents or solvents. This feature simplifies production and waste disposal. Synthesis involves providing an aqueous solution that contains a phosphorus component (e.g., phosphoric acid, phosphate salts such as ammonium phosphate which can be monobasic, dibasic or tribasic salt); an inorganic aluminum containing component (e.g., sodium aluminate, aluminum sulfate, or combinations of these materials); and an inorganic modifying component containing at least one element selected from zirconium, cerium, lanthanum, iron, manganese, cobalt, zinc, and vanadium. Typically, the molar ratios of the starting materials are as follows:

<u>Component</u>	<u>Useful</u>	<u>Preferred</u>
Phosphorus component	0.02-0.90	0.05-0.85
Aluminum containing component	0.02-0.90	0.05-0.85
Inorganic modifying component	0.01-0.50	0.02-0.40

After thoroughly mixing the ingredients, the pH of the aqueous solution is adjusted, with an acid or base, into the range of about 7 to about 12 so that a solid

material (e.g., a homogeneous gel) forms in and precipitates from the solution. After pH adjustment, the aqueous solution may be exposed to hydrothermal or thermal treatment at about 100°C to about 200°C to further facilitate uniform pore formation. After formation, the solid material, which includes the desired aluminophosphate material, can be recovered by any suitable method known in the art, e.g., by filtration. The filtered cake is then washed with water to remove any trapped salt, and then may be contacted with a solution containing ammonium salt or acid to exchange out the sodium ions. Such reduction in the sodium level of is found to increase the hydrothermal stability of the aluminophosphate material. Typically, the sodium level of the final aluminophosphate material should be less than 1.0 wt% Na. After washing and optional exchange, the solid material is dried and calcined.

Although any suitable inorganic modifying component can be used in synthesizing the mesoporous aluminophosphate materials used in the process of the invention, preferably it is a sulfate or a nitrate of zirconium, cerium, lanthanum, manganese, cobalt, zinc, or vanadium.

In the process of the invention, the modified aluminophosphate material is used in the cracking catalyst, preferably as a support in combination with a primary cracking catalyst component and an activated matrix. Other conventional cracking catalyst materials, such as additive catalysts, binding agents, clays, alumina, silica-alumina, and the like, can also be included as part of the cracking catalyst. Typically, the weight ratio of the modified aluminophosphate material to the primary cracking catalyst component is about 0.01 to 0.5, preferably 0.02 to 0.15.

The primary cracking component may be any conventional large-pore molecular sieve having cracking activity and a pore size greater than about 7 Angstrom including zeolite X (U.S. Patent 2,882,442); REX; zeolite Y (U.S. Patent 3,130,007); Ultrastable Y zeolite (USY) (U.S. Patent 3,449,070); Rare Earth exchanged Y (REY) (U.S. Patent 4,415,438); Rare Earth exchanged USY (REUSY); Dealuminated Y (DeAl Y) (U.S. Patent 3,442,792; U.S. Patent 4,331,694); Ultrahydrophobic Y (UHPY) (U.S. Patent 4,401,556); and/or dealuminated silicon-enriched zeolites, e.g., LZ-210 (U.S. Patent 4,678,765). Preferred are higher silica forms of zeolite Y. Zeolite ZK-5 (U.S. Patent 3,247,195);, zeolite ZK-4 (U.S. Patent 3,314,752); ZSM-20 (U.S. Patent 3,972,983);

zeolite Beta (U.S. Patent 3,308,069) and zeolite L (U.S. Patents 3,216,789; and 4,701,315). Naturally occurring zeolites such as faujasite, mordenite and the like may also be used. These materials may be subjected to conventional treatments, such as impregnation or ion exchange with rare earths to increase stability. The preferred large pore molecular sieve of those listed above is a zeolite Y, more preferably an REY, USY or REUSY.

Other suitable large-pore crystalline molecular sieves include pillared silicates and/or clays; aluminophosphates, e.g., ALPO4-5, ALPO4-8, VPI-5; silicoaluminophosphates, e.g., SAPO-5, SAPO-37, SAPO-31, SAPO-40; and other metal aluminophosphates. These are variously described in U.S. Patents 4,310,440; 4,440,871; 4,554,143; 4,567,029; 4,666,875; 4,742,033; 4,880,611; 4,859,314; and 4,791,083.

The cracking catalyst may also include an additive catalyst in the form of a medium pore zeolite having a Constraint Index (which is defined in U.S. Patent No. 4,016,218) of about 1 to about 12. Suitable medium pore zeolites include ZSM-5 (U.S. Patent 3,702,886 and Re. 29,948); ZSM-11 (U.S. Patent 3,709,979); ZSM-12 (U.S. Patent 4,832,449); ZSM-22 (U.S. Patent 4,556,477); ZSM-23 (U.S. Patent 4,076,842); ZSM-35 (U.S. Patent 4,016,245); ZSM-48 (U.S. Patent 4,397,827); ZSM-57 (U.S. Patent 4,046,685); PSH-3 (U.S. Patent 4,439,409); and MCM-22 (U.S. Patent 4,954,325) either alone or in combination. Preferably, the medium pore zeolite is ZSM-5.

The invention will now be more particularly described with reference to the following Examples. In the Examples, pore size distributions are measured by a N<sub>2</sub> desorption process based on ASTM method D4641 and pore volumes are measured by a N<sub>2</sub> adsorption process based on ASTM method D4222, which documents are entirely incorporated herein by reference. The pore volume and pore size distribution data reported herein correspond to pores ranging from approximately 14 to 1000 Å in radius, and do not include any microporous pores which have typically less than 14 Å in radius.

#### **EXAMPLE 1 - Zirconium Aluminophosphate**

##### **A. Production of the Support Material**

A zirconium modified aluminophosphate material was prepared by mixing together, at 40° C, 1700 grams of water, 29 grams of concentrated phosphoric acid, 133



grams of zirconium sulfate, and 170 grams of sodium aluminate. In this mixture, the zirconium/aluminum/phosphorus molar ratio was 0.35/0.5/0.15. After thoroughly mixing these ingredients, the pH of the solution was adjusted to 11 using ammonium hydroxide. The resulting mixture was transferred to a polypropylene bottle and placed in a steam box (100° C) for 48 hours. The mixture was then filtered to separate the solid material from the liquid, and the solid material was washed to provide a wet cake, a portion of which was dried at about 85° C (another portion of this washed material was used in the following test for measuring its hydrothermal stability). A portion of the dried solid material was calcined in air at 540° C for six hours. The resulting zirconium aluminophosphate material had the following properties and characteristics:

<u>Elemental Analysis</u>	<u>Weight Percent</u>
Zr	26.4
Al	24.3
P	4.0
Surface Area - 175 m <sup>2</sup> /g	
Average pore diameter - 41 Å	
Pore volume - 0.21 cc/g	

<u>Pore Size Distribution</u>	<u>Desorption, %</u>
< 50 Å	80%
50 - 100 Å	10%
100 - 150 Å	5%
> 150 Å	5%

#### **B. Hydrothermal Stability Test**

A portion of the wet cake from Example 1A above was slurried with deionized (DI) water (20 g DI water per g of ZrAlPO<sub>x</sub>). The pH of the slurry was adjusted to 4.0 by adding concentrated HCl solution while stirring for 15 minutes. Then the cake was filtered and washed until it was free of residual chloride. The resultant material was dried at 120° C overnight and then air calcined at 540° C for three hours. One portion of this

calcined material was steamed (100% atmospheric pressure steam) at 815° C for 2 hours, and another portion was steamed at 815° C for 4 hours. The surface area of the calcined and steamed materials were as follows:

<u>Material</u>	<u>Surface Area, m<sup>2</sup>/g</u>
Calcined only	227
Steamed for 2 hours	85
Steamed for 4 hours	68

These results demonstrate that the zirconium aluminophosphate material according to the invention is hydrothermally stable and maintains about 30% or more of its surface area under the severe steam deactivating conditions, such as would be experienced in a FCC regenerator. It will also be seen that sodium removal resulting from the acid exchange increased the surface area of the base air calcined material from 175 m<sup>2</sup>/g for the product of Example 1A to 227 m<sup>2</sup>/g for the product of Example 1B.

#### **EXAMPLE 2 - Cerium Aluminophosphate**

##### **A. Production of the Support Material**

A cerium modified aluminophosphate material was prepared by mixing together, at 40° C, 2100 grams of water, 45 grams of concentrated phosphoric acid, 133 grams of cerium sulfate, 75 grams of concentrated sulfuric acid, and 760 grams of sodium aluminate. In this mixture, the cerium/aluminum/phosphorus molar ratio was 1/8/1. After thoroughly mixing these ingredients, the pH of the solution was adjusted to 7 using 50% sulfuric acid. The resulting mixture was transferred to a polypropylene bottle and placed in a steam box (100° C) for 48 hours. The mixture was then filtered to separate the solid material from the liquid, and the solid material was washed to provide a wet cake, a portion of which was dried at about 85° C (another portion of this washed material was used in the following hydrothermal stability test). A portion of this solid material was calcined in air at 540° C for six hours. The resulting cerium aluminophosphate material had the following properties and characteristics:

<u>Elemental Analysis</u>	<u>Weight Percent</u>
Ce	8.6
Al	36.2
P	1.6

Surface Area - 272 m<sup>2</sup>/g

Average pore diameter - 65 Å

Pore volume - 0.50 cc/g

<u>Pore Size Distribution</u>	<u>Desorption, %</u>
< 50 Å	44%
50 - 100 Å	20%
100 - 150 Å	12%
> 150 Å	24%

#### **B. Hydrothermal Stability Test**

A portion of the wet cake from Example 2A above was slurried with deionized (DI) water (20 g DI water per g of CeAlPO<sub>4</sub>). The pH of the slurry was adjusted to 4.0 by adding concentrated HCl solution while stirring for 15 minutes. Then the cake was filtered and washed until it was free of residual chloride. The resultant material was dried at 120° C overnight and then air calcined at 540° C for three hours. One portion of this calcined material was steamed (100% atmospheric pressure steam) at 815° C for 2 hours, and another portion was steamed at 815° C for 4 hours. The surface area of these calcined and steamed materials were as follows:

<u>Material</u>	<u>Surface Area, m<sup>2</sup>/g</u>
Calcined only	272
Steamed for 2 hours	138
Steamed for 4 hours	143

These results demonstrate that the cerium aluminophosphate material according to the invention is hydrothermally stable and maintains greater than 50% of its surface area under these severe steam deactivating conditions.

**EXAMPLE 3 - Cerium Aluminophosphate**

Another cerium modified aluminophosphate material was prepared by mixing together, at 40° C, 2100 grams of water, 360 grams of concentrated phosphoric acid, 135 grams of cerium sulfate, and 100 grams of aluminum sulfate. In this mixture, the cerium/aluminum/phosphorus molar ratio was 1/1/8. After thoroughly mixing these ingredients, the pH of the solution was adjusted to 7 using ammonium hydroxide. The resulting mixture was transferred to a polypropylene bottle and placed in a steam box (100° C) for 48 hours. The mixture was then filtered to separate the solid material from the liquid, and the solid material was washed and dried at about 85° C. This solid material was calcined in air at 540° C for six hours. The resulting cerium aluminophosphate material had the following properties and characteristics:

<u>Elemental Analysis</u>	<u>Weight Percent</u>
Ce	31.4
Al	5.5
P	21.0

Surface Area - 133 m<sup>2</sup>/g

Average pore diameter - 93 Å

Pore volume - 0.31 cc/g

<u>Pore Size Distribution</u>	<u>Desorption, %</u>
< 50 Å	33%
50 - 100 Å	18%
100 - 150 Å	12%
> 150 Å	27%.

**EXAMPLE 4 - Lanthanum Aluminophosphate**

A lanthanum modified aluminophosphate material was prepared as follows. A first solution was prepared by mixing together 2500 grams of water, 90 grams of concentrated phosphoric acid, and 260 grams of lanthanum nitrate. A second solution was prepared by

combining 1670 grams of water and 600 grams of sodium aluminate. These two solutions were combined with stirring. The lanthanum/aluminum/phosphorus molar ratio of this mixture was 1/8/1. After thoroughly mixing these solutions, the pH of the resulting mixture was adjusted to 12 by adding 150 grams of sulfuric acid. The resulting mixture was then transferred to a polypropylene bottle and placed in a steam box (100° C) for 48 hours. Thereafter, the mixture was filtered to separate the solid material from the liquid, and the solid material was washed and dried at about 85° C. This solid material was calcined in air at 540° C for six hours. The resulting lanthanum aluminophosphate material had the following properties and characteristics:

<u>Elemental Analysis</u>	<u>Weight Percent</u>
La	16.6
Al	29.8
P	4.8
Surface Area - 123 m <sup>2</sup> /g	
Average pore diameter - 84 Å	
Pore volume - 0.26 cc/g	
<u>Pore Size Distribution</u>	<u>Desorption, %</u>
< 50 Å	32%
50 - 100 Å	56%
100 - 150 Å	10%
> 150 Å	< 5%

#### **EXAMPLE 5 - Manganese Aluminophosphate**

A manganese modified aluminophosphate material was prepared by mixing together 2100 grams of water, 45 grams of concentrated phosphoric acid, 68 grams of manganese sulfate, and 760 grams of aluminum sulfate. In this mixture, the manganese/aluminum/phosphorus molar ratio was 1/8/1. After thoroughly mixing these ingredients, the pH of the solution was adjusted to 11 by adding ammonium hydroxide. The resulting mixture was transferred to a polypropylene bottle and placed in a steam box (100° C) for 48 hours. The mixture was then filtered to separate the solid material from

the liquid, and the solid material was washed and dried at about 85°C. The solid material was re-slurried with deionized water (20 cc of DI water/g of  $\text{MnAlPO}_x$ ) and the pH of the slurry was adjusted to 4.0 or slightly below with a concentrated HCl solution. The pH was maintained for 15 minutes and filtered to separate the solid material from the liquid. The filter cake was washed thoroughly with 70°C DI water until the washed solution is free of chloride anion, dried overnight at 120°C, and then calcined in air at 540°C for six hours. The resulting manganese aluminophosphate material had the properties and characteristics listed in Table 1.

#### **EXAMPLE 6 - Zinc Aluminophosphate**

A zinc modified aluminophosphate material was prepared by mixing together 2100 grams of water, 45 grams of concentrated phosphoric acid, 115 grams of zinc sulfate, 75 grams of concentrated sulfuric acid, and 760 grams of sodium aluminate. In this mixture, the zinc/aluminum/phosphorus molar ratio was 1/8/1. After thoroughly mixing these ingredients, the pH of the solution was adjusted to 11 by adding 50% sulfuric acid. The resulting mixture was transferred to a polypropylene bottle and placed in a steam box (100°C) for 48 hours. The mixture was then filtered to separate the solid material from the liquid, and the solid material was washed and dried at about 85°C. The solid material was re-slurried with deionized water (20 cc of DI water/g of  $\text{ZnAlPO}_x$ ) and the pH of the slurry was adjusted to 4.0 or slightly below with a concentrated HCl solution. The pH was maintained for 15 minutes and filtered to separate the solid material from the liquid. The filter cake was washed thoroughly with 70°C DI water, dried overnight at 120°C, and then calcined in air at 540°C for six hours. The resulting zinc aluminophosphate material had the properties and characteristics listed in Table 1.

#### **EXAMPLE 7 (Comparative)- Iron Aluminophosphate**

A solution was prepared by mixing 1700 grams of water, 65 grams of concentrated phosphoric acid, 200 grams of ferrous sulfate, and 110 grams of aluminum sulfate. The molar ratio of the iron/aluminum/phosphorous was 0.34/0.33/0.33. The pH of the product was adjusted to 7 with the addition of concentrated ammonium hydroxide. The material was then filtered and washed and dried at ~85°C. A portion of the material was

air calcined to 540°C for six hours. The resulting iron aluminophosphate material had the properties and characteristics listed in Table 1.

Table 1

	<u>ZnAlPO<sub>x</sub></u> <u>Example 5</u> <u>Invention</u>	<u>MnAlPO<sub>x</sub></u> <u>Example 6</u> <u>Invention</u>	<u>FeAlPO<sub>x</sub></u> <u>Example 7</u> <u>Comparative</u>
<u>Calcined Acid Form</u>			
Metal loading, wt%	4.2% Zn	5.7% Mn	21% Fe
Al <sub>2</sub> O <sub>3</sub> , wt%	-	-	12.2
P, wt%	-	-	12.4
Na, wt%	0.22	0.08	0.009
Surface area, m <sup>2</sup> /g	314	244	109
Average pore diameter (Å)	50	44	202
Pore volume (>14Å), cc/g	0.37	0.26	0.55
Pore size distribution, %			
<50 Å	39	75	4
50-100 Å	17	23	12
100-150 Å	9	1	15
>150 Å	35	1	69
<u>Steam Deactivated Catalyst</u> <u>(1500 °F for 4 hrs)</u>			
Surface area, m <sup>2</sup> /g	155	103	6

The results in Table 1 show that ZnAlPO<sub>x</sub> and MnAlPO<sub>x</sub> of the invention retained a surface area in excess of 100 m<sup>2</sup>/g after severe steaming. However, the FeAlPO<sub>x</sub> with a pore size distribution outside the invention lost almost all of its surface area upon steaming.

#### EXAMPLE 8 - Cobalt Aluminophosphate

##### Sample A (Invention)

A solution was prepared by mixing 500 grams of water, 45 grams of concentrated phosphoric acid, 117 grams of cobalt nitrate and 75 grams of concentrated sulfuric acid. Another solution was prepared containing 1600 grams of water and 300 grams of sodium aluminate. These two solutions were combined with stirring. The molar ratio of the

cobalt/aluminum/phosphorous was 1/8/1. The pH of the mixture was adjusted to 9 with the addition of 50% solution of sulfuric acid. The resulting mixture was placed in a polypropylene bottle and put in a steam box (100°C) for 48 hours. The mixture was then filtered and the solid residue was washed and dried at ~85°C. A portion of the residue was air calcined to 540°C for six hours. The elemental analyses and physical properties were as follows:

Element, wt%	
Co	7.1
Al	25.3
P	3.4
Surface Area, m <sup>2</sup> /g	145

A portion of the above material was exchanged four times with a 0.1N solution of ammonium nitrate and the resulting material was then filtered and washed and dried at ~85°C. A portion of the material was air calcined to 540°C for six hours. The resulting cobalt aluminophosphate material had the properties and characteristics listed in Table 2.

#### **Sample B (Invention)**

A solution was prepared by mixing 2100 grams of water, 45 grams of concentrated phosphoric acid, 117 grams of cobalt nitrate, 75 grams of concentrated sulfuric acid, and 300 grams of sodium aluminate. The molar ratio of the cobalt/aluminum/phosphorous was 1/8/1. The pH of the mixture was adjusted to 8 with the addition of 50% solution of sulfuric acid. The resulting mixture was placed in a polypropylene bottle and put in a steam box (100°C) for 48 hours. The mixture was then filtered and the solid residue was washed and dried at ~85°C. A portion of the residue was air calcined to 540°C for six hours. The elemental analyses and physical properties were as follows:

Element, wt%	
Co	6.0
Al	19.2
P	2.6
Surface Area, m <sup>2</sup> /g	114



A portion of the above material was exchanged four times with a 0.1N solution of ammonium nitrate and the resulting material was then filtered and washed and dried at  $\sim 85^{\circ}\text{C}$ . A portion of the material was air calcined to  $540^{\circ}\text{C}$  for six hours. The resulting cobalt aluminophosphate material had the properties and characteristics listed in Table 2.

#### **Sample C (Invention)**

A cobalt modified aluminophosphate material was prepared in the same manner as for Sample B above, except the pH of the mixture was adjusted to 7 with the addition of 50% solution of sulfuric acid. The elemental analyses and physical properties of the product were as follows:

Element, wt%	
Co	6.8
Al	19.6
P	2.9

A portion of the above material was slurried with DI water (20 g DI water per g of  $\text{CoAlPO}_4$ ). The pH of the slurry was adjusted to 4.0 by adding concentrated HCl solution while stirring for 15 minutes. Then the cake was filtered and washed until it was free of residual chloride. The gel was dried at  $120^{\circ}\text{C}$  for overnight and calcined in air at  $538^{\circ}\text{C}$  for 3 hours. The resulting cobalt aluminophosphate material had the properties and characteristics listed in Table 2.

#### **Sample D (Comparative)**

A cobalt modified aluminophosphate material was prepared by mixing 2100 grams of water, 45 grams of concentrated phosphoric acid, 117 grams of cobalt nitrate, 75 grams of concentrated sulfuric acid, and 300 grams of aluminum sulfate. The molar ratio of the cobalt/aluminum/phosphorous was 1/8/1. The pH of the mixture was adjusted to 11 with the addition of concentrated ammonium hydroxide. The resulting mixture was placed in a polypropylene bottle and put in a steam box ( $100^{\circ}\text{C}$ ) for 48 hours. The mixture was then filtered and the solid residue was washed and dried at  $\sim 85^{\circ}\text{C}$ . A portion

of the residue was air calcined to 540°C for six hours. The elemental analyses and physical properties were as follows:

Element, wt%	
Co	10.7
Al	27.4
P	5.8

A portion of the above material was slurried with DI water (20 g DI water per g of  $\text{CoAlPO}_4$ ). The pH of the slurry was adjusted to 4.0 by adding concentrated HCl solution while stirring for 15 minutes. Then the cake was filtered and washed until it was free of residual chloride. The gel was dried at 120°C for overnight and calcined in air at 538°C for 3 hours. The resulting cobalt aluminophosphate material had the properties and characteristics listed in Table 2.

#### Sample E (Comparative)

A cobalt modified aluminophosphate material was prepared from a solution which was prepared with mixing, containing 1700 grams of water, 29 grams of concentrated phosphoric acid, 213 grams of cobalt nitrate, and 170 grams of aluminum sulfate. The molar ratio of the cobalt/aluminum/phosphorous was 0.35/0.5/0.15. The pH of the mixture was adjusted to 7 with the addition of concentrated ammonium hydroxide. The resulting mixture was placed in a polypropylene bottle and put in a steam box (100°C) for 48 hours. The mixture was then filtered and the solid residue was washed and dried at ~85°C. A portion of the residue was air calcined to 540°C for six hours. The elemental analyses and physical properties were as follows:

Element, wt%	
Co	28
Al	10.9
P	6.3

A portion of the above material was slurried with DI water (20 g DI water per g of  $\text{CoAlPO}_4$ ). The pH of the slurry was adjusted to 4.0 by adding concentrated HCl solution

while stirring for 15 minutes. Then the cake was filtered and washed until it was free of residual chloride. The gel was dried at 120°C for overnight and calcined in air at 538°C for 3 hours. The resulting cobalt aluminophosphate material had the properties and characteristics listed in Table 2.

#### Hydrothermal Stability Test of the CoAlPO<sub>x</sub> Samples

The hydrothermal stability of each CoAlPO<sub>x</sub> gel was evaluated by steaming the material at 1500°F (815°C) for 4 hours with 100% steam at atmospheric pressure. The results are given in Table 2 below and Figure 1. The results show that Samples A-C, with the average pore size and pore size distribution according to the invention, exhibited excellent hydrothermal stability in that they maintained over 100 m<sup>2</sup>/g surface area even after severe steaming. In contrast, Samples D and E, without the narrowly-defined mesopores structure of the invention, lost nearly all of their surface area upon steaming at 1500°F.

**Table 2**

Sample	A	B	C	D	E
Calcined Acid Form					
Co loading, wt%	6.2	7.9	10	15	28
Al <sub>2</sub> O <sub>3</sub> , wt%	47.8	36	51	18	20
P, wt%	3.4	2.6	4	11	10
Na, wt%	0.49	0.28	0.05	0.01	0.01
Surface area, m <sup>2</sup> /g	321	247	175	103	82
Average pore diameter (Å)	67	74	74	152	108
Pore volume (>14Å), cc/g	0.55	0.44	0.37	0.38	0.24
Pore size distribution, %					
<50 Å	38	29	32	8	13
50-100 Å	32	39	27	14	27
100-150 Å	9	11	13	14	19
>150 Å	21	21	28	64	41
Steam Deactivated Catalyst (1500°F for 4 hrs)					
Surface area, m <sup>2</sup> /g	128	113	111	29	18

**EXAMPLE 9 -Vanadium Aluminophosphate****Sample F**

A solution was prepared by mixing 2100 grams of water, 45 grams of concentrated phosphoric acid, 87 grams of vanadyl sulfate, 75 grams of concentrated sulfuric acid and 760 grams of sodium aluminate. The molar ratio of the vanadium/aluminum/ phosphorous was 1/8/1. The pH of the mixture was adjusted to 7 with the addition of 50% sulfuric acid. The mixture was then filtered and the solid residue washed and dried at about 85°C. A portion of the dried material was air calcined to 540°C for six hours. The elemental analyses and physical properties of resulting vanadium aluminophosphate material were as follows:

Element, wt%	
V	3.0
Al	17.0
P	1.7
Surface Area, m <sup>2</sup> /g	335

A further portion of the above dried material was slurried with DI water (20 g DI water per g of VAlPO<sub>4</sub>). The pH of the slurry was adjusted to 4.0 by adding concentrated HCl solution while stirring for 15 minutes. Then the cake was filtered and washed until it was free of residual chloride. The gel was dried at 120°C for overnight and calcined in air at 538°C for 3 hours. The resulting vanadium aluminophosphate material had the properties and characteristics listed in Table 3.

**Sample G**

A solution was prepared by mixing 2100 grams of water, 45 grams of concentrated phosphoric acid, 87 grams of vanadyl sulfate, 75 grams of concentrated sulfuric acid and 760 grams of sodium aluminate. The molar ratio of the vanadium/aluminum/ phosphorous was 1/8/1. The pH of the mixture was adjusted to 8 with the addition of 50% solution of sulfuric acid. The elemental analyses and physical properties of the resulting vanadium aluminophosphate material were as follows:

Element, wt%	
V	2.1
Al	20.9
P	1.2
Surface Area, m <sup>2</sup> /g	130

A further portion of the above dried material was exchanged four times with a 0.1N solution of ammonium nitrate to remove the excess sodium, and the resultant product was then filtered and the residue washed and dried at about 85°C. A portion of the residue was air calcined to 540°C for six hours. The resulting vanadium aluminophosphate material had the properties and characteristics listed in Table 3.

The calcined acid form of each of the VAIPO<sub>x</sub> Samples F and G were subjected to the steam deactivation test described above and the results are summarized in Table 3.

Table 3

	<u>VAIPO<sub>x</sub></u> <u>Sample F</u> <u>Invention</u>	<u>VAIPO<sub>x</sub></u> <u>Sample G</u> <u>Invention</u>
<u>Calcined Acid Form</u>		
V loading, wt%	3.0	2.1
Al <sub>2</sub> O <sub>3</sub> , wt%	39	35.6
P, wt%	1.2	0.3
Na, wt%	0.59	0.83
Surface area, m <sup>2</sup> /g	317	304
Average pore diameter (Å)	53	36
Pore volume (>14Å), cc/g	0.42	0.27
Pore size distribution, %		
<50 Å	55	82
50-100 Å	20	10
100-150 Å	6	2
>150 Å	19	6
Steam Deactivated Catalyst (1500F for 4 hrs)		
Surface area, m <sup>2</sup> /g	81	126

The results in Table 3 show that Samples F and G, with the average pore size and pore size distribution according to the invention, exhibited excellent hydrothermal stability. Sample G prepared under higher pH conditions exhibited better stability in that it maintained over 100 m<sup>2</sup>/g surface area even after severe steaming.

#### **EXAMPLE 10 - Fluid Catalytic Cracking with ZrAlPO<sub>x</sub>**

##### **A. Preparation of a ZrAlPO<sub>x</sub> Material**

A thermally stable, high surface area, mesoporous ZrAlPO<sub>x</sub> material was prepared as described above in Example 1. The described wet cake of ZrAlPO<sub>x</sub> was used for the catalyst preparations that follow.

##### **B. Preparation of a USY/ZrAlPO<sub>x</sub>/Clay Catalyst**

A first catalyst, Catalyst A, was prepared using commercial Na-form USY zeolite with a silica to alumina ratio of 5.4 and a unit cell size of 24.54 Å. The Na-form USY was slurried and ball milled for 16 hours. A wet cake of the ZrAlPO<sub>x</sub> material above was slurried in deionized water, and the pH of the resultant slurry was adjusted to 4 using concentrated HCl. The ZrAlPO<sub>x</sub> material was then filtered, washed, and ball milled for 16 hours.

A uniform physical mixture of the milled USY slurry, the milled ZrAlPO<sub>x</sub> slurry, binding agent, and kaolin clay was prepared. The final slurry contained 21% USY, 25% ZrAlPO<sub>x</sub>, 7% binding agent, and 47% clay, on a 100% solids basis. The mixture was spray-dried to fine spherical particles with approximately 70 μ average particle diameter. The sprayed product was then air calcined, followed by ammonium exchange using an ammonium sulfate solution. The exchanged catalyst was further washed with deionized water, dried overnight, and calcined at 538°C for three hours. The properties of the final catalyst are shown in Table 4.

##### **C. Preparation of a USY/Alumina/Clay Catalyst**

A second catalyst, Catalyst B, was prepared following the procedure in Example 10B, above, except that the ZrAlPO<sub>x</sub> in Catalyst A was replaced with HCl-peptized alumina. The peptized alumina gel was prepared from pseudoboehmite alumina powder

that was peptized with HCl solution for 30 minutes (at 12 wt% solids). The properties of Catalyst B also are shown in Table 4.

**D. Preparation of a USY/ZrAlPO<sub>x</sub>/Alumina/Clay Catalyst**

A third catalyst, Catalyst C, was prepared following the procedure in Example 10B, above, except that the amount of ZrAlPO<sub>x</sub> was reduced and part of the clay was replaced with the HCl-peptized alumina used in Example 10C so that the spray dried slurry contained 21% USY, 15% ZrAlPO<sub>x</sub>, 25% alumina, 7% binding agent, and 32% clay, on a 100% solids basis. The final properties of Catalyst C are shown in Table 4.

**E. Preparation of a USY/ZrAlPO<sub>x</sub>/Alumina/Clay Catalyst**

A fourth catalyst, Catalyst D, was prepared following the procedure in Example 10D, above, except that the ZrAlPO<sub>x</sub> in Catalyst C was replaced with HCl-peptized ZrAlPO<sub>x</sub> gel, prepared by peptization of wet cake using HCl solution. The properties of Catalyst D also are shown in Table 4.

Before evaluating the catalysts for performance on a pilot unit for catalytic cracking, each catalyst was deactivated at 1450° F and 35 psig for 20 hours using 50% steam and 50% air. The surface areas of the steamed catalysts are shown in Table 4.

**TABLE 4**

Compositional Feature	Catalyst A 25% ZrAlPO <sub>x</sub> and No Alumina	Catalyst B 25% Alumina and No ZrAlPO <sub>x</sub>	Catalyst C 15% Ball Milled ZrAlPO <sub>x</sub> (Replaced Part of Clay) and 25% Alumina	Catalyst D 15% Peptized ZrAlPO <sub>x</sub> (Replaced Part of Clay) and 25% Alumina
<b>Calcined Catalyst Properties</b>				
Rare Earth wt. %	1.7	1.9	1.9	1.8
Na wt. %	0.1	0.1	0.1	0.1
SiO <sub>2</sub> wt. %	37.1	36.7	29.6	30.3
Al <sub>2</sub> O <sub>3</sub> wt. %	42.5	52.0	51.6	54.2
Surface Area m <sup>2</sup> /g	221	222	255	256
<b>Steam Deactivated Catalyst Properties</b>				
Surface Area m <sup>2</sup> /g	--	123	122	120

**F. Catalytic Cracking Process**

Catalysts B through D were compared for catalytic cracking activity in a fixed-fluidized-bed ("FFB") reactor at 935°F, using a 1.0 minute catalyst contact time on a Arab Light Vacuum Gas Oil. The feedstock properties are shown in Table 5 below:

**TABLE 5**

Charge Stock Properties	Vacuum Gas Oil
Gravity at 60° F	0.9010
Refractive Index	1.50084
Aniline Point, ° F	164
CCR, wt. %	0.90
Hydrogen, wt. %	11.63
Sulfur, wt. %	2.8
Nitrogen, ppm	990
Basic nitrogen, ppm	250
<b>Distillation</b>	
IBP, ° F	536
50 wt. %, ° F	868
99.5 wt. %, ° F	1170

These catalysts were then used in the FFB pilot plant. The catalyst performances are summarized in Table 6, where product selectivity was interpolated to a constant conversion, 65 wt. % conversion of feed to 430° F material.



TABLE 6

	Catalyst B	Catalyst C	Catalyst D
Matrix	No Added ZrAlPO <sub>x</sub>	+ 15% Ball Milled ZrAlPO <sub>x</sub>	+ 15% Peptized ZrAlPO <sub>x</sub>
Conversion, wt. %	65	65	65
Cat/Oil	3.8	3.3	3.6
C <sub>5</sub> <sup>+</sup> Gasoline, wt. %	39.6	42.1	42.4
LFO, wt. %	25.4	25.6	25.5
HFO, wt. %	9.6	9.4	9.5
Coke, wt. %	5.1	5.3	5.1
RON, C <sub>5</sub> <sup>+</sup> Gasoline	88.2	85.7	85.6
H <sub>2</sub> S, wt. %	1.7	1.8	1.9
C <sub>1</sub> + C <sub>2</sub> Gas, wt. %	1.8	1.8	1.7
Total C <sub>3</sub> Gas, wt. %	6.3	4.9	4.9
Total C <sub>4</sub> Gas, wt. %	10.4	8.9	8.8
C <sub>3</sub> <sup>+</sup> /total C <sub>3</sub>	0.81	0.80	0.80
C <sub>4</sub> <sup>+</sup> /total C <sub>4</sub>	0.48	0.48	0.50
C <sub>4</sub> <sup>+</sup> /C <sub>3</sub> <sup>+</sup>	0.98	1.10	1.13

The test results in Table 6 demonstrate that incorporation of ZrAlPO<sub>x</sub> into the zeolite matrix resulted in significantly improved gasoline yields (as much as 2.8 wt. %). This increase in gasoline yields for Catalysts C and D resulted mostly from lower C<sub>3</sub> and C<sub>4</sub> yields. The ZrAlPO<sub>x</sub> matrix "as-is" (Catalyst C) had a slightly higher coke-making tendency, but this tendency was alleviated by HCl peptization of the gel (Catalyst D).

The ZrAlPO<sub>x</sub> matrix has bottoms cracking activity, and a slight decrease in HFO (heavy fuel oil) yield is observed (0.2%). The bottoms yield differences are small for these catalysts, probably because all three catalysts convert nearly all of the crackable heavy ends at this conversion level. One negative aspect of the ZrAlPO<sub>x</sub> containing catalyst is the lower research octane number ("RON") of the produced gasoline, lowered by as much as 2.6.

The  $\text{ZrAlPO}_x$  containing catalysts increased the  $\text{H}_2\text{S}$  yield by >10%, suggesting that this material may have potential for  $\text{SO}_x$  removal and/or gasoline sulfur removal. The  $\text{ZrAlPO}_x$  containing catalysts increased the butylene selectivity in  $\text{C}_4$  gas and the  $\text{C}_4$  olefin-to- $\text{C}_3$  olefin ratio. The results in Table 6 clearly show that the chemistry of  $\text{ZrAlPO}_x$  is different from a typical active alumina matrix, which is usually added to improve bottoms cracking.

#### **EXAMPLE 11 - Fluid Catalytic Cracking with $\text{CeAlPO}_x$**

##### **A. Preparation of a $\text{CeAlPO}_x$ Material**

A thermally stable, high surface area, mesoporous  $\text{CeAlPO}_x$  material was prepared as described above in Example 2. The wet cake of  $\text{CeAlPO}_x$  described above was used for the catalyst preparations that follow.

##### **B. Preparation of a USY/ $\text{CeAlPO}_x$ /Clay Catalyst**

A first catalyst, Catalyst E, was prepared using commercial Na-form USY zeolite with a silica to alumina ratio of 5.4 and a unit cell size of 24.54 Å. The Na-form USY was slurried and ball milled for 16 hours. A wet cake of the  $\text{CeAlPO}_x$  material above was slurried in deionized water, and the pH of the resultant slurry was adjusted to 4 using concentrated HCl. The  $\text{CeAlPO}_x$  material was then filtered, washed, and ball milled for 16 hours.

A uniform physical mixture of the milled USY slurry, the milled  $\text{CeAlPO}_x$  slurry, binding agent, and kaolin clay was prepared. The final slurry contained 21% USY, 25%  $\text{CeAlPO}_x$ , 7% binding agent, and 47% clay, on a 100% solids basis. The mixture was spray-dried to fine spherical particles with approximately 70  $\mu$  average particle diameter. The sprayed product was then air calcined, followed by ammonium exchange using an ammonium sulfate solution. The exchanged catalyst was further washed with deionized water, dried overnight, and calcined at 538°C for three hours. The properties of the final catalyst are shown in Table 7.

##### **C. Preparation of a USY/Alumina/Clay Catalyst**

A second catalyst, Catalyst F, was prepared following the procedure in Example 11B, above, except that the  $\text{CeAlPO}_x$  in Catalyst E was replaced with HCl-peptized pseudoboehmite alumina. The properties of Catalyst F also are shown in Table 7.

**D. Preparation of a USY/CeAlPO<sub>x</sub>/Alumina/Clay Catalyst**

A third catalyst, Catalyst G, was prepared following the procedure in Example 11B, above, except that the amount of CeAlPO<sub>x</sub> was reduced and part of the clay was replaced with the HCl-peptized alumina used in Example 11C so that the spray dried slurry contained 21% USY, 15% CeAlPO<sub>x</sub>, 25% alumina, 7% binding agent, and 32% clay, on a 100% solids basis HCl-peptized pseudoboehmite alumina. The final properties of Catalyst G are shown in Table 7.

**E. Preparation of a USY/CeAlPO<sub>x</sub>/Alumina/Clay Catalyst**

A fourth catalyst, Catalyst H, was prepared following the procedure in Example 11D, above, except that the CeAlPO<sub>x</sub> in Catalyst G was replaced with HCl-peptized CeAlPO<sub>x</sub>. The properties of Catalyst H also are shown in Table 7.

Before evaluating the catalysts for performance on a pilot unit for catalytic cracking, each catalyst was deactivated at 1450° F and 35 psig for 20 hours using 50% steam and 50% air. The surface areas of the steamed catalysts are shown in Table 7.

**TABLE 7**

	Catalyst E	Catalyst F	Catalyst G	Catalyst H
Compositional Feature	25% CeAlPO <sub>x</sub> and No Alumina	25% Alumina and No CeAlPO <sub>x</sub>	15% Ball Milled CeAlPO <sub>x</sub> (Replaced Part of Clay) and 25% Alumina	15% Peptized CeAlPO <sub>x</sub> (Replaced Part of Clay) and 25% Alumina
<b>Calcined Catalyst Properties</b>				
Rare Earth wt. %	4.9	1.9	3.7	3.5
Na wt. %	0.1	0.1	0.1	0.2
SiO <sub>2</sub> wt. %	38.1	36.7	31.0	30.6
Al <sub>2</sub> O <sub>3</sub> wt. %	46.5	52.0	57.9	55.5
Surface Area m <sup>2</sup> /g	238	222	249	257
<b>Steam Deactivated Catalyst Properties</b>				
Surface Area m <sup>2</sup> /g	90	123	130	126

**F. Catalytic Cracking Process**

Catalysts E and F were compared for use in a catalytic cracking process using an FFB reactor at 935°F, having a 1.0 minute catalyst contact time using Arab Light Vacuum Gas Oil. The feedstock had the properties described in Table 5 above.

The performances of the catalysts are summarized in Table 8, where product selectivity was interpolated to a constant conversion, 65 wt.% conversion of feed to 430° F material.

TABLE 8

	Deactivated Catalyst E	Deactivated Catalyst F
Matrix	25% CeAlPO <sub>x</sub>	25% Activated Al <sub>2</sub> O <sub>3</sub>
Conversion, wt. %	65	65
Cat/Oil	4.1	3.8
C <sub>1</sub> + C <sub>2</sub> Gas, wt. %	2.0	1.8
Total C <sub>3</sub> Gas, wt. %	5.4	6.3
Total C <sub>4</sub> Gas, wt. %	9.5	10.4
C <sub>5</sub> <sup>+</sup> Gasoline, wt. %	40.7	39.6
LFO, wt. %	25.0	25.4
HFO, wt. %	10.0	9.6
Coke, wt. %	5.5	5.1
RON, C <sub>5</sub> <sup>+</sup> Gasoline	87.6	88.2

The results in Table 8 suggest that the CeAlPO<sub>x</sub> matrix has bottoms cracking activity comparable to that of the activated alumina matrix. The catalysts provided comparable HFO yields. The CeAlPO<sub>x</sub> catalyst shows higher gasoline selectivity (1.1 wt.% yield advantage).

#### G. Product Selectivity Improvement With Addition of CeAlPO<sub>x</sub>

Catalysts G and H were compared with Catalyst F to determine the benefits of adding CeAlPO<sub>x</sub> to an FCC catalyst. An FFB reactor was used with the Arab Light Vacuum Gas Oil described above in Table 5. The performances of the catalysts are

summarized in Table 9, where product selectivity was interpolated to a constant conversion, 65 wt.% conversion of feed to 430° F material.

TABLE 9

Matrix	Catalyst F No Added CeAlPO <sub>x</sub>	Catalyst G + 15% Ball Milled CeAlPO <sub>x</sub>	Catalyst H + 15% Peptized CeAlPO <sub>x</sub>
Conversion, wt. %	65	65	65
Cat/Oil	3.8	3.6	3.5
C <sub>5</sub> <sup>+</sup> Gasoline, wt. %	39.6	40.7	42.0
LFO, wt. %	25.4	25.0	25.3
HFO, wt. %	9.6	10.0	9.7
Coke, wt. %	5.1	5.5	5.2
RON, C <sub>5</sub> <sup>+</sup> Gasoline	88.2	87.8	85.5
H <sub>2</sub> S, wt. %	1.7	1.9	1.9
C <sub>1</sub> + C <sub>2</sub> Gas, wt. %	1.8	1.8	1.7
Total C <sub>3</sub> Gas, wt. %	6.3	5.4	5.0
Total C <sub>4</sub> Gas, wt. %	10.4	9.5	9.1
C <sub>3</sub> <sup>+</sup> /total C <sub>3</sub>	0.81	0.81	0.80
C <sub>4</sub> <sup>+</sup> /total C <sub>4</sub>	0.48	0.52	0.49
C <sub>4</sub> <sup>+</sup> /C <sub>3</sub> <sup>+</sup>	0.98	1.11	1.13

The test results in Table 9 demonstrate that incorporation of CeAlPO<sub>x</sub> into the matrix resulted in significantly improved gasoline yields (as much as 2.4 wt.%). The increase in gasoline yields for Catalysts G and H resulted mostly from lower C<sub>3</sub> and C<sub>4</sub> yields. The CeAlPO<sub>x</sub> matrix "as-is" (Catalyst G) had a slightly higher coke-making tendency, but this tendency was alleviated by HCl peptization of the gel (Catalyst H).

The bottoms yields are comparable for all three catalysts, probably because all three catalysts convert nearly all of the crackable heavy ends at this conversion level. One negative aspect of the CeAlPO<sub>x</sub> containing catalyst is that it lowered the research octane number ("RON") of the produced gasoline by as much as 2.7.

The CeAlPO<sub>x</sub> containing catalysts increased the H<sub>2</sub>S yield by >10%, suggesting that this material may have potential for SO<sub>x</sub> removal and/or gasoline sulfur removal. The CeAlPO<sub>x</sub> containing catalysts increased the butylene selectivity in C<sub>4</sub> gas, and the C<sub>4</sub> olefin-to-C<sub>3</sub> olefin ratio. The results in Table 9 clearly show that the chemistry of CeAlPO<sub>x</sub> is different from a typical active alumina matrix, which is usually added to improve bottoms cracking.

#### EXAMPLE 12 - Fluid Catalytic Cracking Evaluation of CoAlPO<sub>x</sub> and VAIPO<sub>x</sub>

CoAlPO<sub>x</sub> from Example 8 (Sample A) and VAIPO<sub>x</sub> from Example 9 (Sample F) were each pelleted and sized to an average particle size of approximately 70 micrometer (μ), then steamed in a muffle furnace at 1500°F for 4 hours to simulate catalyst deactivation in an FCC unit. Ten weight percent of steamed pellets were blended with an equilibrium catalyst from an FCC unit. The equilibrium catalyst has very low metals level (120 ppm V and 60 ppm Ni).

The additives were tested for gas oil cracking activity and selectivity using an ASTM microactivity test (ASTM procedure D-3907). The vacuum gas oil feed stock properties are shown in a Table 10 below.

**Table 10**

<i>Charge Stock Properties</i>	<i>Vacuum Gas Oil</i>
API Gravity	26.6
Aniline Point, °F	182
CCR, wt%	0.23
Sulfur, wt%	1.05
Nitrogen, ppm	600
Basic nitrogen, ppm	310
Ni, ppm	0.32
V, ppm	0.68
Fe, ppm	9.15
Cu, ppm	0.05
Na, ppm	2.93
Distillation	
IBP, °F	358
50wt%, °F	716
99.5%, °F	1130

A range of conversions was scanned by varying the catalyst-to-oil ratios and reactions were run at 980°F. Gasoline range product from each material balance was analyzed with a GC equipped with a sulfur detector (AED) to determine the gasoline sulfur concentration. To reduce experimental errors in sulfur concentration associated with fluctuations in distillation cut point of the gasoline, S species ranging only from thiophene to C4-thiophenes were quantified using the sulfur detector and the sum was defined as "cut-gasoline S". The sulfur level reported for "cut-gasoline S" excludes any benzothiophene and higher boiling S species which were trapped in a gasoline sample due to distillation overlap. Performances of the catalysts are summarized in Table 11, where the product selectivity was interpolated to a constant conversion, 65wt% or 70wt% conversion of feed to 430°F material.

Table 11

	<i>Base Case</i>	<i>+ 10% CoAlPO<sub>x</sub></i>	<i>+ 10% VAlPO<sub>x</sub></i>
Conversion, wt%	70	70	70
Cat/Oil	3.2	3.2	3.7
H <sub>2</sub> yield, wt%	0.04	+0.24	+0.21
C <sub>1</sub> + C <sub>2</sub> Gas, wt%	1.4	+0.3	+0
Total C <sub>3</sub> Gas, wt%	5.4	+0.1	-0.2
C <sub>3</sub> <sup>=</sup> yield, wt%	4.6	+0	-0.1
Total C <sub>4</sub> Gas, wt%	11.1	-0.2	-0.4
C <sub>4</sub> <sup>=</sup> yield, wt%	5.4	-0.1	+0.1
iC <sub>4</sub> yield, wt%	4.8	-0.2	-0.4
C <sub>3</sub> <sup>+</sup> Gasoline, wt%	49.3	-1.7	-0.9
LFO, wt%	25.6	-0.4	+0.1
HFO, wt%	4.4	+0.4	-0.1
Coke, wt%	2.5	+1.4	+1.3
Cut Gasoline S, PPM	445	330	383
% Reduction in Cut Gasoline S	Base	26.0	13.9
% Reduction in Gasoline S, Feed Basis	Base	28.5	15.4

Data in Table 11 show that the gasoline S concentration was reduced by 26% by addition of CoAlPO<sub>x</sub>, and 13.9% by the addition of VAlPO<sub>x</sub>. The overall FCC yields (C<sub>1</sub>-C<sub>4</sub> gas production, gasoline, LCO, and bottoms yields) changed only slightly with the CoAlPO<sub>x</sub> and VAlPO<sub>x</sub> addition, although some increases in H<sub>2</sub> and coke yields were observed. When the desulfurization results were recalculated to incorporate the gasoline-volume-loss, CoAlPO<sub>x</sub> gave 29% S reduction and VAlPO<sub>x</sub> gave 15% reduction.



**EXAMPLE 13 - Fluid Catalytic Cracking Evaluation of ZnAlPO<sub>4</sub>**

ZnAlPO<sub>4</sub> from Example 6 was pelleted and sized to an average particle size of approximately 70 micrometer ( $\mu$ ), then steamed in a muffle furnace at 1500°F for 4 hours to simulate catalyst deactivation in an FCC unit. Ten weight percent of steamed ZnAlPO<sub>4</sub> pellets were blended with a steam deactivated, Super Nova D<sup>TR</sup> FCC catalyst obtained from W. R. Grace. Performances of the ZnAlPO<sub>4</sub> are summarized in Table 12.

**Table 12**

	<u>Base Case</u>	<u>+ 10% ZnAlPO<sub>4</sub></u>
Conversion, wt%	72	72
Cat/Oil	3.2	3.6
H <sub>2</sub> yield, wt%	0.09	+0.03
C <sub>1</sub> + C <sub>2</sub> Gas, wt%	1.8	+0.2
Total C <sub>3</sub> Gas, wt%	5.8	+0.3
C <sub>3</sub> <sup>=</sup> yield, wt%	4.9	+0.2
Total C <sub>4</sub> Gas, wt%	11.3	+0.1
C <sub>4</sub> <sup>=</sup> yield, wt%	5.9	-0.2
iC <sub>4</sub> yield, wt%	4.5	+0.2
C <sub>3</sub> <sup>+</sup> Gasoline, wt%	50.0	-1.0
LFO, wt%	23.7	+0
HFO, wt%	4.3	-0.2
Coke, wt%	2.9	+0.4
Cut Gasoline S, PPM	477	449
% Reduction in Cut Gasoline S	Base	5.9
% Reduction in Gasoline S, Feed Basis	Base	7.7

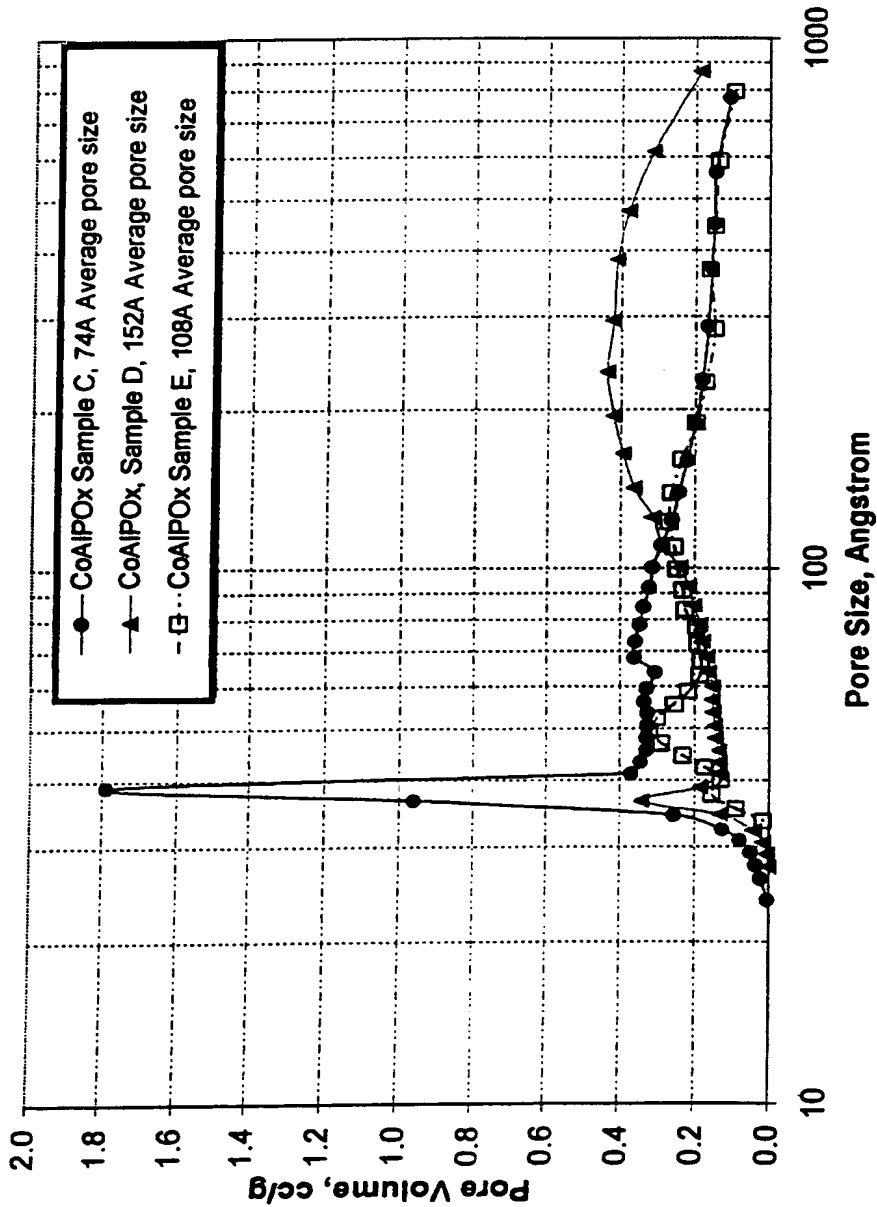
It will be seen from Table 12 that gasoline sulfur concentration was reduced by 6% by addition of the  $\text{ZnAlPO}_x$ . The overall FCC yields ( $\text{H}_2$ ,  $\text{C}_1$ -  $\text{C}_4$  gas production, gasoline, LCO, and bottoms yields) changed only slightly with the  $\text{ZnAlPO}_x$  addition, although some increase in coke yield was observed. When the desulfurization results were recalculated to incorporate the gasoline-volume-loss,  $\text{ZnAlPO}_x$  gave 8% S reduction.

**WHAT IS CLAIMED IS:**

1. A process for catalytic cracking of a hydrocarbon feedstock comprising contacting the feedstock with a catalyst composition comprising a mesoporous aluminophosphate material which comprises a solid aluminophosphate composition modified with at least one element selected from zirconium, cerium, lanthanum, manganese, cobalt, zinc, and vanadium, wherein the mesoporous aluminophosphate material has a specific surface of at least  $100 \text{ m}^2/\text{g}$ , an average pore diameter less than or equal to  $100 \text{ \AA}$ , and a pore size distribution such that at least 50% of the pores have a pore diameter less than  $100 \text{ \AA}$ .
2. The process of claim 1 wherein the mesoporous aluminophosphate material has an average pore diameter of 30 to  $100 \text{ \AA}$ .
3. The process of claim 1 wherein the mesoporous aluminophosphate material has a specific surface area of at least  $175 \text{ m}^2/\text{g}$ .
4. The process of claim 1 wherein the mesoporous aluminophosphate material has a pore volume in the range from  $0.10 \text{ cc/g}$  to  $0.75 \text{ cc/g}$ .
5. The process of claim 1 wherein the catalyst composition further comprises a primary catalytically active cracking component.
6. The process of claim 5 wherein the weight ratio of the aluminophosphate material to the primary cracking catalyst component is about 0.01 to 0.5.
7. The process of claim 5 wherein the primary catalytically active cracking component comprises a large pore molecular sieve having a pore size greater than about 7 Angstrom.
8. The process of claim 7 wherein the primary catalytically active cracking component comprises a zeolite Y.

9. The process of claim 1 wherein the hydrocarbon feedstock contains sulfur and the process produces a gasoline boiling range product having a lower sulfur content than the feedstock.

Figure 1  
N2 Pore Size Distribution



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/33999**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : C10G 29/02, 29/04, 11/02

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/114, 120.01, 120.05, 120.1, 120.25, 120.35, 292, 248, 249, 244

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST

search terms: large pore, aluminophosphate, cracking

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,456,821 A (ABSIL ET AL) 10 October 1995 (10/10/95), See abstract, lines 1-4 and 7-9, column 5, lines 19-25, column 6, lines 51-61 and column 7, lines 10-20.	1-9
Y	US 5,888,378 A (KOWALSKI) 30 March 1999 (30/03/99), See abstract and column 3, lines 10-45.	1-9
Y	US 3,271,299 A (KEARBY) 06 September 1966 (06/09/66), See column 1, lines 10-20 and 36-40, and column 2, lines 49-51 and 63-70.	1-9
Y	US 3,904,550 A (PINE) 09 September 1975 (09/09/75), See abstract and column 3, lines 26-36 and 48-58.	1-9

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier document published on or after the international filing date	"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

11 FEBRUARY 2001

Date of mailing of the international search report

04 APR 2001

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

B. Stauder  
NADINE PREISCH

Telephone No. (703) 308-0661

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US00/33999

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,584,091 A (PINE) 22 April 1986 (22/04/86), See entire document.	1-9
A	US 5,972,203 A (SMITH ET AL) 26 October 1999 (26/10/99), See entire document.	1-9

**INTERNATIONAL SEARCH REPORT**

International application No.

**PCT/US00/33999**

**A. CLASSIFICATION OF SUBJECT MATTER:**

US CL :

208/114, 120.01, 120.05, 120.1, 120.25, 120.35, 292, 248, 249, 244



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**